

Some Rules for $S(-2k)$ Dipole Sums?

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Stieltjes conditions and the ratio test provide necessary but not sufficient conditions on $S(-2k)$ dipole sums. If the dipole sums are accurate the associated $[n, n-1]$ Padé approximant provides a better representation of $\alpha(\omega)$, the frequency-dependent dipole polarizability, than a truncated series expression and, in addition, should bound $\alpha(\omega)$ below. It is shown how constraints on the dipole sums effect the form of the $[2, 1]$ Padé approximant and an additional constraint is derived that ensures the analyticity of the approximant on $0 \leq \omega < \omega_1$. There then follows a discussion of the reliability of available literature dipole sum values for small molecules containing H, C, N and O.

Key words: Dipole sums – Padé approximants.

1. Introduction

The dipole oscillator sums $S(-2k)$ [1], $k = 1, 2, \dots$, or Cauchy coefficients, are the coefficients of the Cauchy power series representation of the frequency-dependent dipole polarizability, $\alpha(\omega)$,

$$\alpha(\omega) = \sum_{k=0}^{\infty} S(-2k-2)\omega^{2k}. \quad (1)$$

Thus, a knowledge of the dipole sums of a system will provide information on optical properties and interaction coefficients related to $\alpha(\omega)$.

This paper attempts to address the problem of how to decide if a given set of dipole sums is reasonable or not. We are led to discuss this since literature values for some small molecular systems can differ and, therefore, it is desirable to find criteria to select which set is the most reliable.

It is well known that $\alpha(i\omega)$ is a series of Stieltjes and as a consequence, the coefficients in Eq. (1) should satisfy the determinantal relationships

$$D(n, m) > 0 \quad m = 0, 1, \dots; n = -1, 0, \dots \quad (2)$$

where

$$D(n, m) = \begin{vmatrix} S(-2n-2) & S(-2n-4) & \cdots & S(-2n-2m-2) \\ S(-2n-4) & S(-2n-6) & \cdots & S(-2n-2m-4) \\ \vdots & \vdots & \ddots & \vdots \\ S(-2n-2m-2) & S(-2n-2m-4) & \cdots & S(-2n-4m-2) \end{vmatrix}.$$

Clearly any sums, however determined, should satisfy these conditions. Considering the electronic dispersion region only and ignoring infra-red contributions, (assuming separability these can be incorporated later; see, for example, [3]) it follows that $\alpha(\omega)$ is analytic for $0 \leq \omega < \omega_1$ and singular at $\omega = \omega_1$ where ω_1 is the first allowed dipole transition. Hence, the radius of convergence of Eq. (1) will be ω_1 and from the ratio test

$$\frac{S(-2n)}{S(-2n-2)} \geq \omega_1^2 \quad n = 1, 2, 3, \dots \quad (3)$$

Given a set of the first M dipole sums, rather than using Eq. (1) and truncating after M terms it should be a better procedure to use the associated Padé approximant [2]. This is because the latter will include some estimate of the higher order terms. In addition, if the sums are accurate,

$$[n, n-1] \leq \alpha(\omega) \quad (4)$$

i.e. the $[n, n-1]$ Padé approximant underestimates the higher order contributions [2]. However, if the sums used to form the Padé approximant are inaccurate, Eq. (4) may be violated and/or the truncated series may be a better representation.

Here we consider cases where the dipole sums are known to $S(-8)$ and we show, in a straightforward fashion, how the constraints of Eqs. (2) and (3) affect the form of the $[2, 1]$ Padé approximant. First, however, we derive an additional constraint that ensures the analyticity of the Padé approximant on $0 \leq \omega < \omega_1$ before discussing some other possible pointers to the reliability or otherwise of the dipole sums.

2. The $[2,1]$ Padé Approximant

Given the $S(-2k)$ through $S(-8)$, the $[2,1]$ Padé approximant can be obtained in the form

$$[2,1] = (a_0 + a_1\omega^2)/(1 + b_1\omega^2 + b_2\omega^4) \quad (5)$$

where the coefficients may be determined in terms of the sums by making Eqs. (1) and (5) agree to order ω^6 . It is often more convenient to rewrite Eq. (5) as

$$[2, 1] = \frac{f_a}{\omega_a^2 - \omega^2} + \frac{f_b}{\omega_b^2 - \omega^2} \quad (6)$$

where $\{f_i, \omega_i\}$ are effective oscillator strengths and transition frequencies, respectively.

To obtain constraints on the constants in Eqs. (5) and (6), two possible approaches are available. Starting with Eq. (5) the determinantal conditions can be used; for example, in the case of b_1 we can write

$$b_1 = [S(-8)S(-2) - S(-6)S(-4)]/[S(-4)^2 - S(-2)S(-6)]. \quad (7)$$

The condition $D(n, 1) > 0$ ensures the monotonicity of the sequence of ratios

$$S(-2n)/S(-2n-2) > S(-2n-2)/S(-2n-4) \quad (8)$$

and this, with $n = 1$ and $n = 2$, implies $b_1 < 0$. Similarly $b_2 > 0$, $a_0 = S(-2)$ and $-a_1 < Nb_2$ where N is the number of electrons.

Alternatively it is possible to begin with Eq. (6) and impose the conditions:

$$f_a > 0, f_b > 0, \omega_a^2 > 0, \omega_b^2 > 0 \quad (9)$$

so that Eq. (6) represents a monotonic decreasing function of $i\omega$. For Eq. (4) to be satisfied as $\omega \rightarrow \infty$ we require, further, that

$$f_a + f_b \leq N. \quad (10)$$

We should emphasise that these two approaches are entirely equivalent, i.e. Eqs. (9) and (10) imply the determinantal constraints of Eq. (2) to terms involving $S(-8)$ and vice-versa.

In many respects, however, it can be easier to work from Eq. (6). For example, we obtain

$$S(-2n-2) = f_a \omega_a^{-2n-2} + f_b \omega_b^{-2n-2} \quad (11)$$

from which it is easy to deduce that

$$R_n = S(-2n)/S(-2n-2) \quad (12)$$

is a monotonic decreasing sequence with limit ω_a^2 (taking $\omega_a < \omega_b$), c.f. Eq. (3). It is also possible to show that, after a certain value of n (which may be $n = 1$ or even $n = 0$) the differences $R_n - R_{n+1}$ become monotonic decreasing.

The majority of these conditions derive from the fact that $\alpha(i\omega)$ is a series of Stieltjes, i.e. depend on a very general property of α . The only criterion which is characteristic of the individual atom or molecule under consideration follows from the fact that the first pole of $\alpha(\omega)$ occurs at $\omega = \omega_1$. If the sums used to find the $[2, 1]$ Padé approximant are accurate, we know from Eq. (4) that $[2, 1] \leq \alpha(\omega)$ on $[0, \omega_1]$ so that

$$\omega_a \geq \omega_1. \quad (13)$$

Since ω_a will depend on the dipole sums, this constraint imposes conditions on these sums which can be used to test the sum values if ω_1 is known. These conditions are:

$$R_2 \frac{R_1 - R_3}{R_2 - R_3} \geq \omega_1^2 \quad (14)$$

$$\begin{vmatrix} \omega_1^4 & \omega_1^2 & 1 \\ S(-2) & S(-4) & S(-6) \\ S(-4) & S(-6) & S(-8) \end{vmatrix} \geq 0. \quad (15)$$

3. Values for Dipole Sums from the Literature for Molecules Containing H, C, N and O

A number of techniques are available for use in an attempt to obtain reliable $S(-2k)$ values [2–15]. These include a variety of semi-empirical methods as well as purely theoretical procedures which have been applied to atoms [4] and, in particular, the inert gases. For all but the simplest systems and regardless of whether they have been determined theoretically or semi-empirically the values obtained possess some inherent errors [5].

In the case of molecules, the most reliable sum values are found by the construction of dipole oscillator strength distributions (DOSD) [9, 10], however, this is a considerable and time consuming task. More simply empirical fits can be made to refractivity data to determine $\alpha(\omega)$ from which the sums are extracted via Eq. (1). Errors arise due to limitations in the accuracy of the experimental measurements and the range over which they are taken. Further errors can be introduced in the use of Eq. (1) since the coefficients depend on the number of terms kept in the truncated power series [16]. This is because the terms excluded are effectively taken to be zero and so the remaining terms have to compensate for this.

Table 1 lists literature values of $S(-2k)$ for a number of molecules. These are calculated by well-respected methods but different calculations on the same molecules can give disturbingly different results. We now discuss whether it is possible to assess the accuracy of these various results. The criteria used fall into two classes: theoretical ones which follow from fundamental properties and purely empirical ones which seem to be satisfied by the majority of calculated sums.

(i) The determinantal relations:

These are given by Eq. (2). Many authors have stressed the need to include these constraints when the $S(-2k)$ are determined. All the values obtained from fits to refractive index data given in Table 1 [2, 3, 14, 15] have incorporated this and hence satisfy these relations. The DOSD sum values [9, 10] all satisfy the Stieltjes conditions as well, but were not constrained to do so. However, it is clear from the

Table 1. Literature dipole sum values for molecules containing H, C, N and O atoms^a

| Molecule ^b | $S(0)$ | $S(-2)$ | $S(-4)$ | $S(-6)$ | $S(-8)$ |
|-----------------------|--------|---------|---------|---------|---------|
| H ₂ [9] | 2 | 5.428 | 19.96 | 82.94 | 367.0 |
| [2] | 2 | 5.439 | 20.02 | 81.61 | 350.0 |
| N ₂ [9] | 14 | 11.74 | 30.11 | 101.8 | 384.6 |
| [2] | 14 | 11.74 | 30.17 | 99.21 | 374 |
| O ₂ [9] | 16 | 10.59 | 34.75 | 237.1 | 2196 |
| [2] | 16 | 10.60 | 36.97 | 132.0 | 480 |
| NO [9] | 15 | 11.52 | 38.46 | 276.2 | 3194 |
| [14] | 15 | 11.52 | 39.05 | 246 | 4190 |
| CO [15] | 14 | 13.09 | 47.84 | 318.6 | 2800 |
| CO ₂ [3] | 22 | 17.56 | 49.23 | 235 | 1200 |
| N ₂ O [9] | 22 | 19.70 | 72.11 | 410.7 | 2847 |
| H ₂ O [9] | 10 | 9.642 | 35.42 | 240.1 | 2299 |
| NH ₃ [9] | 10 | 14.56 | 71.44 | 684.0 | 9527 |
| CH ₄ [10] | 10 | 17.27 | 62.41 | 298.3 | 1714 |

^a In atomic units [19].^b Literature source in parenthesis.

table that these relations by themselves do not preclude very different sets of sum values being obtained for a given molecule.

(ii) Conditions involving the first electronic transition frequency ω_1 :

These are given by Eqs. (3), (14) and (15). Where accurate values of ω_1 (either experimental or theoretical) are known, these conditions should surely be included as constraints in the same way as the determinantal conditions. Unfortunately, for molecules larger than diatomics there are severe problems in obtaining experimental estimates for ω_1 , since spectral resolution is complicated by overlapping vibrational and rotational bands [17] (see footnotes to Table 2). Nevertheless, in Table 2 we have listed what we believe to be the most likely values of ω_1 . In the same table are listed $\omega_a, \omega_b, f_a, f_b$ obtained from the [2, 1] Padé approximants. For comparison we also give the single frequency and oscillator strength, ω'_a and f'_a respectively, taken from the [1, 0] Padé approximant; the [1, 0] approximant is, of course, found by using $S(-2)$ and $S(-4)$ only.

Given that the ω_1 values are correct, then Eqs. (3), (14) and (15) are satisfied by all the entries in the table with the single exception of the NO results of Nielson et al. [14] which, therefore, must be regarded with suspicion. We make the empirical observation that ω'_a typically has a value around 0.55 while ω_a has a much reduced value which is quite close to ω_1 . However, in all but one case, $\omega_a - \omega_1 > 0.03$ so ω_a is not too close to ω_1 . A comparison of ω'_a, ω_a and ω_1 suggests that the Langhoff-Karplus sums for O₂ lead to a value for ω_a which is anomalously high and to a lesser extent the same is true for Pack's CO₂ sums and Zeiss and Meath's N₂O and O₂ values. Effectively if $\omega_a < \omega_1$, or is very close to it, then the sums are providing too large a contribution when placed in an $[n, n-1]$ Padé approximant and if $\omega_a \gg \omega_1$ it is likely they are providing a contribution that is too small.

Table 2. Effective oscillator strengths and transition frequencies from the Padé approximants^a

| Molecule | Experi- mental ^{b,c} ω_1 | From [1, 0] | | From [2, 1] | | $f_a + f_b$ | N_b | N | C_6^z | |
|----------------------|--|-------------|--------|-------------|--------|-------------|-------|-----|----------------|----------------|
| | | ω'_a | f'_a | ω_b | f_a | | | | Upper Bound | Lower Bound |
| H ₂ [9] | 0.4110 | 0.5215 | 1.48 | 0.4641 | 0.7340 | 1.0131 | 2 | 2 | 12.19 | 12.02 |
| [2] | | 0.5212 | 1.48 | 0.4736 | 0.7441 | 0.8822 | | | 12.17 | 11.99 |
| N ₂ [9] | 0.4487 | 0.6244 | 4.58 | 0.5025 | 0.9690 | 5.3138 | 10 | 14 | 79.20 | 71.37 |
| [2] | | 0.6238 | 4.57 | 0.4929 | 0.8531 | 4.8201 | | | 78.08 | 69.54 |
| O ₂ [9] | 0.2249 | 0.5520 | 3.23 | 0.3166 | 0.8044 | 5.4413 | 12 | 16 | 75.09 | 56.29 |
| [2] | | 0.5355 | 3.04 | 0.5121 | 0.6200 | 2.0330 | | | 46.67 | 45.43 |
| NO [9] | 0.2014 | 0.5473 | 3.45 | 0.2740 | 0.6979 | 4.9710 | 11 | 15 | 85.73 | 62.79 |
| [14] | | 0.5431 | 3.40 | 0.1940 | 0.5808 | 0.0078 | | | 81.58 | 56.75 |
| CO [15] | 0.2950 | 0.5231 | 3.58 | 0.3231 | 0.7452 | 5.5350 | 10 | 14 | 97.80 | 78.93 |
| CO ₂ [3] | 0.3089 ^d | 0.5972 | 6.26 | 0.4411 | 1.5073 | 19.8237 | 16 | 22 | 191.6 | 190.7 |
| N ₂ O [9] | 0.2503 ^e | 0.5227 | 5.38 | 0.3662 | 0.7673 | 7.6468 | 16 | 22 | 210.8 | 174.3 |
| H ₂ O [9] | 0.2753 ^f | 0.5217 | 2.62 | 0.3042 | 0.6942 | 3.7965 | 8 | 10 | 52.81 | 41.84 |
| NH ₃ [9] | 0.2102 | 0.4515 | 2.97 | 0.2522 | 0.5989 | 4.3667 | 8 | 10 | 102.6 | 83.12 |
| CH ₄ [10] | 0.3132 | 0.5260 | 4.78 | 0.3905 | 0.6769 | 5.3242 | 8 | 10 | 137.2 | 126.7 |

^a All values in atomic units [19].^b Values for diatomics from Ref. [20]; values for polyatomics from Ref. [21].^c Another set of values for ω_1 can be obtained from the pseudostate excitation energies of Ref. [22]. These are obtained using an unpublished fitting procedure so that the dipole sums of [9, 10] are reproduced. They are as follows: $\omega_1(\text{H}_2) = 0.4201$, $\omega_1(\text{N}_2) = 0.4675$, $\omega_1(\text{O}_2) = 0.2576$, $\omega_1(\text{NO}) = 0.2028$, $\omega_1(\text{N}_2\text{O}) = 0.2153$, $\omega_1(\text{H}_2\text{O}) = 0.2558$, $\omega_1(\text{NH}_3) = 0.2154$, $\omega_1(\text{CH}_4) = 0.3211$. Since this representation can be thought of in terms of a [10, 9] Padé approximant, the first pseudo state excitation energies given here should lie just above the true ω_1 , given that the dipole sums from which they are obtained are exact. This is the case with the ω_1 values in the table apart from values for N₂O and H₂O.^d Support for this value is given in Refs. [23–25]. However, there is evidence of a possible very weakly absorbing state at a lower value [23, 25].^e Support for this value is given in Refs. [23, 26, 27]. Again there is the possibility of a lower, weakly absorbing state [23, 27]. See also footnote (c).^f See footnote (c).^g Starkschall and Gordon [5] have also provided molecular interaction coefficient values for like interactions between O₂, N₂O and H₂. However, they only provide molecular sum values for H₂ to S(-6) and so have not been included in this study.

(iii) Effective oscillator strengths:

These should satisfy the condition:

$$f'_a < f_a + f_b < N \quad (16)$$

which they do. Indeed except for H_2 and CO_2 the second inequality can be replaced by \ll . Because transitions involving inner shell electrons are of very high energy, it is to be expected that such transitions have a minute effect on the value of $\alpha(\omega)$ for small ω and so their contribution to the sum values is probably not included when the latter are determined empirically, for example from refractive index measurements at low frequencies. Therefore, in the inequality of Eq. (16) it should be possible to replace N by N_v , the number of valence electrons. This is confirmed by the values in Table 2; usually, in fact, $f_a + f_b \approx \frac{1}{2}N_v$, although there are a few cases where $f_a + f_b$ is a little larger. There are two cases, Langhoff and Karplus's O_2 results and the NO results of Nielson et al., where $f_a + f_b$ is rather low, and where f'_a and $f_a + f_b$ are almost identical. It will be recalled that the same results led to anomalous ω_a values. However, the major cause for concern in Table 2 is the fact that $f_a + f_b$ for CO_2 is almost equal to N . We find it difficult to believe that this can be correct.

(iv) The ratios R_n :

The R_n , given by Eq. (12), form a monotonic decreasing sequence ensured by the condition $D(n, 1) > 0$. An empirical point to note is that for all DOSD sum values $D(n, 1)$, $n = -1, 0, 1$, is monotonic increasing whereas the values of Langhoff and Karplus for O_2 and N_2 are not. By forming the ratios R_n it can be seen that for both Langhoff and Karplus' O_2 and Pack's CO_2 values R_3 is quite far from ω_1^2 and the differences $R_2 - R_3$ are small contrary to the general trend. On the other hand, for the NO sums found by Nielson et al., R_3 is already very close to ω_1^2 . Except for these values R_3 is near ω_1^2 but with $R_3 - \omega_1^2 > 0.03$. In all cases the differences $R_n - R_{n+1}$ are monotonic decreasing for $n = 0$ onwards.

4. Bounds to Dispersion Interaction Coefficients

Normally the most useful application of the effective oscillator strengths and transition frequencies $\{f_i, \omega_i\}$ is in the calculation of lower bounds to dipole dispersion coefficients C_6, γ_3, d_4 . Also, upper bounds can be found by determining similar quantities $\{\bar{f}_i, \bar{\omega}_i\}$ obtained from Padé approximants to the function $\beta = N + \omega^2 \alpha(\omega)$ [18]. In the case of the upper bounds the effective oscillator strengths are constrained to sum to N , i.e. $\bar{f}_a + \bar{f}_b = N$.

Table 2 gives upper and lower bounds to C_6 (for interactions between identical molecules) obtained via the various sum values. It must be stressed that the nomenclature is misleading since the bounds are true bounds only in so far as the sum values are correct. Any errors in the latter can mean that the bounding properties no longer hold and the exact C_6 values can lie outside the calculated bounds. This is shown clearly by the O_2 results: one set of sums implies $45 < C_6 < 47$ and another that $56 < C_6 < 75$. They cannot both be correct.

If we accept most of the values for C_6 , then it is clear that the use of sums up to $S(-8)$ does not give very tight bounds, and it is doubtful if the determination of higher order sums can be sufficiently accurate to improve the situation. Therefore, the calculation of C_6 values via sums and Padé approximants which seemed to promise very accurate results on the basis of those obtained for atoms has proved much less successful when applied to molecules. In view of this those sets of sum values which lead to very tight bounds must be treated with reserve. These are precisely those which lead to abnormal values for $\omega_a, f_a + f_b$ and R_n .

Several points made in Sects. 3 and 4 have already been mentioned previously by Zeiss and Meath [9]. Here we have presented them in a mathematical way whereas they have discussed them in a more physical context.

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References

1. Hirschfelder, J. O., Byers Brown, W., Epstein, S. T.: *Advan. Quantum. Chem.* **1**, 255 (1964)
2. Langhoff, P. W., Karplus, M.: *J. Opt. Soc. Am.* **59**, 863 (1969)
3. Pack, R. T.: *J. Chem. Phys.* **61**, 2091 (1974)
4. Cummings, F. E.: *J. Chem. Phys.* **63**, 4960 (1975)
5. Starkschall, G., Gordon, R. G.: *J. Chem. Phys.* **54**, 663 (1971)
6. Dalgarno, A., Morrison, I. H., Pengelly, R. M.: *Intern. J. Quantum Chem.* **1**, 161 (1967)
7. Thomas, G. F., Meath, W. J.: *A.I.Ch.E. J.* **25**, 352 (1979)
8. Dalgarno, A., Kingston, A. E.: *Proc. Roy. Soc.* **A259**, 424 (1960)
9. Zeiss, G. D., Meath, W. J.: *Mol. Phys.* **33**, 1155 (1977)
10. Thomas, G. F., Meath, W. J.: *Mol. Phys.* **34**, 113 (1977)
11. Margenau, H.: *Phys. Rev.* **37**, 1425 (1931)
12. Margenau, H.: *Phys. Rev.* **56**, 1000 (1939)
13. Dalgarno, A., Kingston, A. E.: *Proc. Phys. Soc.* **72**, 1053 (1958)
14. Neilson, G. C., Parker, G. A., Pack, R. T.: *J. Chem. Phys.* **64**, 2055 (1976).
15. Parker, G. A., Pack, R. T.: *J. Chem. Phys.* **64**, 2010 (1976)
16. Gerhart, D. E.: *J. Chem. Phys.* **62**, 821 (1975).
17. Robin, M. B.: *Higher excited states of polyatomic molecules*, Vol. 1 New York: Academic Press 1974
18. Langhoff, P. W., Karplus, M. in: *The Padé approximant in theoretical physics*, G. A. Baker, Jr. and J. L. Gammel, Eds., Chpt. 2. New York: Academic Press 1970
19. Shull, H., Hall, G. G.: *Nature* **184**, 1559 (1959)
20. Herzberg, G.: *Spectra of diatomic molecules*. New York: D. van Nostrand 1966
21. Herzberg, G.: *Electronic spectra and electronic structure of polyatomic molecules*. New York: D. van Nostrand. 1966
22. Margoliash, D. J., Meath, W. J.: *J. Chem. Phys.* **68**, 1426 (1978)
23. Ashfold, M. N. R., Macpherson, M. T., Simons, J. P.: *Topics Curr. Chem.* **86**, 1 (1979)
24. Rabalais, J. W., McDonald, J. M., Scherr, V., McGlynn, S. P.: *Chem. Rev.* **71**, 73 (1971)
25. Hall, R. I., Chutjian, A., Trajmar, S.: *J. Phys.* **B6**, L264 (1973)
26. Peyerimhoff, S. D., Buenker, R. J.: *J. Chem. Phys.* **49**, 2473 (1968), and references cited therein
27. Hall, R. I., Chutjian, A., Trajmar, S.: *J. Phys.* **B6**, L365 (1973)